



Revealing the ZrO₂ crystal effect of Pd/ZrO₂ catalyst for toluene combustion: A combined DRIFTS and DFT study

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ABSTRACT

The effect of ZrO₂ crystalline phases on Pd/ZrO₂ for catalytic combustion of toluene was investigated. It was found that Pd/t-ZrO₂ showed superior activity when the toluene concentration was lower than 2000 ppm, while Pd/m-ZrO₂ performed better with toluene concentration higher than 3000 ppm. Kinetic studies showed that the reaction order of toluene on Pd/t-ZrO₂ and Pd/m-ZrO₂ is 0 and 2, respectively. The catalytic activity was controlled by combined effect of PdO activity and quantity, which was correlated with the interaction between palladium and zirconia. The t-ZrO₂ increased PdO species activity, while m-ZrO₂ could enhance the amount of PdO. DFT results showed that the p-band center of the O of PdO on t-ZrO₂ was higher, suggesting that PdO was more active. *In situ*-DRIFTS revealed that the reaction pathway of catalytic oxidation of toluene on Pd/ZrO₂ was as follows: toluene was oxidized stepwise to benzyl alcohol, benzaldehyde, benzoic acid, CO₂ and H₂O.

1. Introduction

VOCs (Volatile Organic Compounds) refer to a variety of organic compounds that are gaseous at room temperature, with the boiling points of 50–260 °C, which could result in ozone depletion and photochemical smoke that were harmful to human health and crop growth [1]. Many strategies have been devoted to eliminating VOCs. The catalytic combustion technology was regarded as one of the most promising methods because of its simplicity, secure, low energy consumption and high efficiency [2–8]. Extensive attention has been paid to Pd-based [9–15] catalysts for VOC combustion, mainly because Pd plays a dual role in the reaction processes: Pd site is active for the decomposition of VOCs and Pd oxide provides the surface oxygen source of the catalyst.

Supports, in supported Pd-based catalysts, as key components of catalysts, not only play an important role in the dispersion of the active sites, but also modify the catalytic activity via tuning the interaction between active sites and supports, etc. [12,16–20]. The roles of support on the Pd-based catalysts have been extensively studied, i.e., CeO₂ [21–24], SiO₂ [20,25,26], Al₂O₃ [27,28] and ZrO₂ [29–34]. Miller et al. [32] found the catalytic activity of the supported Pd-based catalyst for methane oxidation. The activity of the catalysts depended on the amount of PdO–oxygen vacancy (Pd), which was in relation to the stability of PdO. The order of catalytic activity was Pd/Al₂O₃ >

Pd/ZrO₂–CeO₂ > Pd/CeO₂, which was consistent with the weak interaction between palladium and supports (Al₂O₃ < ZrO₂–CeO₂ < CeO₂). Meanwhile, supports could also influence the mechanical stability, resistance to toxicity and hydrothermal stability of the catalysts [35]. Araya et al. discovered that Pd/ZrO₂ catalyst showed higher water-resistance than Pd/SiO₂ catalyst [36]. Similar results were also reported by Park et al. [33]. They found that Pd/ZrO₂ catalysts exhibited higher activity and better stability in the presence of water vapor compared with Pd/Al₂O₃. Compared with other supports in Pd-based catalysts, from a practical point of view, ZrO₂ was regarded as a promising carrier for further application.

The textural properties, acidity, and crystal structures of ZrO₂ will affect the catalytic performance. Shin et al. [31] found that lower surface area of ZrO₂ in Pd/ZrO₂ catalysts could induce the formation of larger PdO particles, which showed higher activity than small PdO particles. Zhang et al. [29] prepared ZrO₂ with different crystallinities by pyrolysis of UiO-66 at distinct temperatures for catalytic oxidation of CO. The higher activity was related to the higher ratio of O_{ads}/O_{lat} species and Pd⁰/Pd²⁺ on Pd/ZrO₂ catalysts, which was in relation to the proportion of tetragonal /monoclinic phase in mixed crystalline phases. Zheng et al. [34] studied the effect of crystal forms of ZrO₂ on the hydrodechlorination of chlorobenzene. They found that the catalytic performance of Pd/m-ZrO₂ was better than Pd/t-ZrO₂, which was owing

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to higher dispersion and content of Pd species that led to stronger interaction between metal and support. However, only few studies were reported on the effect of crystal phases of ZrO_2 on Pd/ ZrO_2 for the catalytic combustion of VOCs.

In this study, we investigated the differences in the performance of Pd/ ZrO_2 catalysts with different crystalline of ZrO_2 for toluene catalytic combustion. To gain insights into the structure-performance relationship in the catalysts, the kinetic studies, surface properties (XPS and H_2 -TPR), and DRIFTS were used to understand the effects of ZrO_2 crystalline on Pd/ ZrO_2 for toluene combustion.

2. Experimental

2.1. Chemicals

The chemical reagents used in the experiment were purchased from Aladdin Chemical and Energy Chemical, and the chemical purity was Analytical Reagent.

2.2. Catalyst preparation

Zirconia with different crystal phases (tetragonal zirconia and monoclinic zirconia) were synthesized by hydrothermal method [37]. Typically, zirconium nitrate and urea were first dissolved in deionized water to form 50 mL aqueous solution ($[\text{Zr}] = 0.4 \text{ mol/L}$, $[\text{urea}]: [\text{Zr}] = 10: 1$). The solution was then introduced to a 100 mL self-pressurized stainless steel hydrothermal kettle lined with Teflon, and then placed in an oven at 200°C for 6 h. The resultant solid was washed by centrifugation with deionized water for 1–3 times until the supernatant was neutral. The obtained material after centrifugation was dried in an oven at 110°C overnight, and then calcined at 400°C for 4 h. The obtained powder was denoted as m- ZrO_2 . Tetragonal zirconia (t- ZrO_2) was prepared with the similar procedure as m- ZrO_2 , except that anhydrous methanol was dissolved zirconium nitrate and urea instead of water.

Pd/ ZrO_2 was prepared via wet impregnation method. Typically, 0.99 g ZrO_2 (m- ZrO_2 or t- ZrO_2) was added in 20 mL H_2O . Then 1 mL Pd (NO_3)₂ aqueous solution (10 mg Pd/mL) was added into the solution with vigorous stirring for 24 h at room temperature. The solvent was removed by a rotary evaporator at 60°C for 1 h. The resultant powder was dried overnight in an oven at 110°C and then calcined in air at 500°C for 6 h. The obtained samples were denoted as Pd/m- ZrO_2 and Pd/t- ZrO_2 .

2.3. Catalytic activity test

The catalytic performance and kinetic studies were measured in a U-shaped quartz tube reactor (diameter 4 mm) under toluene + O_2 + N_2 with different toluene and oxygen concentrations, as our previous report [38]. In a typical test, the catalyst was pretreated with 20 vol% O_2/N_2 for 30 min at 400°C . The catalyst was cooled to room temperature, and then the feed gas was introduced into the reactor. The reaction temperature was then increased from room temperature to 400°C with a step of 10°C and each temperature was held for 30 min to ensure that the reaction reached the steady state. The effluent gas was analyzed using a GC-7820 gas chromatograph. The formula for the toluene oxidation rate or reaction rate is as follows:

$$r = \frac{c \times X \times F}{V \times m}$$

Where r , c , X , F , V , and m represent toluene reaction rate, toluene concentration, toluene conversion ratio, gas volume flow rate, molar volume of gas and catalyst quality, respectively.

2.4. Characterization of the catalysts

Transmission electron microscope (TEM) images were obtained with a Talos F200X Lorenz with an acceleration voltage of 200 kV. The measured samples were sonicated and dispersed in water, and the solution was dropped on a fine carbon film and left for 12 h at room temperature. The carbon film was then scanned and photographed. Inductively coupled plasma mass spectrometer (ICP-MS) was used to measure the content of palladium. Nitrogen adsorption and desorption isotherms were measured using a Belsorp-Max instrument. Samples were degassed in a vacuum of 200°C for 2 h prior to measurement. The surface area was determined by Brunauer-Emmett-Teller (BET) method, and the pore size distribution was calculated by Barrett-Joyner-Halenda method. The X-ray diffraction (XRD) pattern was measured with the XRD-6100 equipment manufactured in Shimadzu, Japan, which has a maximum power of 3 kW. The scanning rate was $7^\circ/\text{min}$ and the scanning range was $10\text{--}80^\circ$. X-ray photoelectron spectroscopy (XPS) was obtained with Thermo Fisher ESCALAB Xi+ equipment, using the adventitious carbon at 284.6 eV as the internal standard to calibrate the binding energy.

The oxygen storage capacity (OSC) and oxygen release rate (ORR) of the catalysts were measured using a NETZSCH-STA449F5 thermal gravimetric analyzer. Before measurement, the samples were first pretreated in a 20 % O_2/Ar atmosphere at 400°C to remove impurities. Then the temperature was decreased to a certain temperature, the two atmospheres of 10 % H_2/Ar and 20 % O_2/Ar were switched with three or four times until the weight change remain the same.

$$\text{OSC}(\mu\text{mol/g}) = -\frac{W_{\text{oxi-red}}}{W_{\text{cat}} \times n_{\text{O}}}$$

$$\text{ORR}(\mu\text{mol}/(\text{g} \bullet \text{s})) = -\frac{DTG_{\text{max-red}}}{W_{\text{cat}} \times n_{\text{O}}}$$

Where $W_{\text{oxi-red}}$ represents the weight differential of the catalyst under oxidative atmosphere and reductive atmosphere; W_{cat} is the mass of the catalyst when put into the crucible; $DTG_{\text{max-red}}$ is the maximum slope of weight loss curve of catalyst in reducing atmosphere; n_{O} is the atomic mass of oxygen.

In-situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) was measured with a Nicolet iS50 device to detect some intermediates or functional groups in the reaction process. DRIFTS was obtained in the range of $650\text{--}4000 \text{ cm}^{-1}$ with a resolution of 4 cm^{-1} by accumulating 32 scans. The temperature was controlled by the Pike temperature module, and the raw gas was controlled by the mass flow controller. The catalyst was pretreated for 1 h in a 20 vol% $\text{O}_2 + \text{N}_2$ (40 mL/min) stream at 400°C , and the background spectrum was deducted in N_2 stream at 150°C . The experiment details were the same as our previously work [38].

2.5. Computational details

The spin-polarized density functional theory (DFT) calculations were implemented by using the Vienna ab-initio Simulation Package (VASP) [39]. Projection-augmented wave (PAW) pseudopotential was used to represent core electrons with a cutoff energy of 400 eV [40]. Perdew Burke Ernzerhof (PBE) [41] and generalized gradient approximation (GGA) were used to calculate the exchange correlation potential. Partial density of states (PDOS) curve was calculated using LOBSTER [42]. The $7 \times 7 \times 7$ and $8 \times 8 \times 6$ k -point mesh sampling grid were used in the bulk of m- ZrO_2 and t- ZrO_2 , respectively. A $1 \times 1 \times 1$ k -point mesh sampling grid was used in the surfaces system. A monoclinic ZrO_2 cell of $5.15 \times 5.21 \times 5.31 \text{ \AA}$ and a tetragonal ZrO_2 cell of $3.64 \times 3.64 \times 3.64 \text{ \AA}$ were optimized, which were in good agreement with the experimental results [31]. The m- ZrO_2 ($\bar{1}11$) and t- ZrO_2 (101) surface systems which are the most stable surfaces of thermodynamics

were chosen to build a rhombic supercell of $6.71 \times 7.30 \times 17.91 \text{ \AA}$ and a cuboid supercell of $6.31 \times 7.17 \times 16.71 \text{ \AA}$, respectively. The bottom-two atomic layers of the slab were fixed and other layers were relaxed. The vacuum space of both systems was set as 12 \AA . In order to build a suitable catalyst model, a single Pd atom was adsorbed on the top surface of ZrO_2 , and an O atom was connected to the top of the Pd atom. The convergence tolerance for self-consistent field tolerance and threshold of forces on atoms are set as 10^{-5} eV and 0.02 eV/\AA , respectively.

The energy of O dissociation from O-Pd/ ZrO_2 system (E_{des}) was calculated as follows.

$$E_{\text{des}} = E_{\text{Pd/ZrO}_2} - E_{\text{O-Pd/ZrO}_2} + E_{\text{O}}$$

where $E_{\text{Pd/ZrO}_2}$ and $E_{\text{O-Pd/ZrO}_2}$ are the total energy of Pd/ ZrO_2 system and O-Pd/ ZrO_2 system, respectively. E_{O} is total energy of $1/2\text{O}_2$.

For quantitative comparison, energy-weighted average ε (p-band center) was used as the descriptor of these projection bands:

$$\varepsilon = \frac{\sum PDOS(E_i) \cdot E_i}{\sum PDOS(E_i)}$$

where $\sum PDOS(E_i)$ is the PDOS in an energy range $[E_i, E_i + \Delta E]$ (ΔE was a value of 0.05 eV). For O, the sum over the highest occupied 2 s and 2 p states fall into range of -10 – 0 eV [42].

3. Results and discussion

3.1. Crystalline structures and morphology

Fig. 1A shows the XRD patterns of Pd/m- ZrO_2 , m- ZrO_2 , Pd/t- ZrO_2 and t- ZrO_2 . All the diffraction peaks on Pd/t- ZrO_2 and Pd/m- ZrO_2 were ascribed to tetragonal zirconia (JCPDS 37-1484) and monoclinic zirconia (JCPDS 50-1089), respectively. No peak of palladium in the Pd/ ZrO_2 spectrum was observed, indicating that palladium did not exist on the carrier in the form of a crystal. The grain size calculated by Scherrer equation and the grain size of Pd/t- ZrO_2 and Pd/m- ZrO_2 are 5.3 and 6.9 nm, respectively.

The N_2 adsorption-desorption isotherms of Pd/ ZrO_2 and ZrO_2 are shown in Fig. 1B and Fig. S1, respectively. The isotherms of physical adsorption and desorption of all the catalysts can be assigned to IV isotherms with H3-type [29]. Table 1 lists the specific surface area, average pore size and pore volume of Pd/ ZrO_2 catalysts. The specific surface areas of Pd/m- ZrO_2 and Pd/t- ZrO_2 are 109 and $96 \text{ m}^2/\text{g}$, respectively. The pore volumes of Pd/m- ZrO_2 and Pd/t- ZrO_2 were 0.19 and 0.16 mL/g and the average pore sizes of Pd/m- ZrO_2 and Pd/t- ZrO_2 were 6.8 and 5.1 nm, respectively. The structures of the two mesoporous

Table 1

Physicochemical parameters of the catalysts.

Catalyst	S_{BET} (m^2/g)	Pore volume (mL/g)	Mean pore diameter (nm)	D^* (nm)	$O_{\text{ads}}/$ O_{lat}^b (%)	$\text{Pd}^{2+}/$ Pd^b (%)	Pd content ^c (mg/g)
Pd/m- ZrO_2	109	0.19	6.8	6.6	14	47	10
Pd/t- ZrO_2	96	0.16	5.1	5.8	10	37	10

^a The crystal sizes of catalysts were calculated by Scherrer equation in XRD.

^b Calculated according to the corresponding peak area in XPS.

^c Measured by inductively coupled plasma mass spectrometer (ICP-MS).

materials nearly identical. In addition, no difference in physical properties was found between the ZrO_2 support and Pd/ ZrO_2 .

Fig. 2 shows the TEM images of Pd/m- ZrO_2 and Pd/t- ZrO_2 . The sizes of these catalysts are 6.7 and 5.8 nm respectively. The size of the lattice fringes on Pd/m- ZrO_2 were 0.32, 0.28 and 0.18 nm, which corresponded to the (111), (111) and (022) of the ZrO_2 monoclinic crystal, respectively. Similarly, for Pd/t- ZrO_2 , the sizes of its lattice fringes were 0.26, 0.18 and 0.30 nm, which were ascribed to (110), (112) and (011). The EDS composition analysis diagrams of Pd/m- ZrO_2 and Pd/t- ZrO_2 indicated that Pd was distributed on the carrier ZrO_2 with high dispersion, which was consistent with the XRD results.

3.2. Catalytic performance

The blank experiment was first carried with only quartz sand without catalysts. No measurable reaction rate was observed in the investigated reaction temperature of 100 – $400 \text{ }^\circ\text{C}$. Figs. 3A and 3B show the catalytic performance of Pd/t- ZrO_2 and Pd/m- ZrO_2 at various toluene concentrations as a function of temperature, respectively. The toluene conversion with respect to temperature shows an S-shaped curve. For Pd/t- ZrO_2 , the toluene conversion decreased with increasing toluene concentration. The opposite phenomenon was observed on Pd/m- ZrO_2 . The specific data of toluene conversion rate at different temperatures and toluene concentrations are shown in Table S2. At $220 \text{ }^\circ\text{C}$, the oxidation rates of toluene on Pd/t- ZrO_2 and Pd/m- ZrO_2 at 1000 ppm were 29.7 and $6.6 \text{ } \mu\text{mol (g}_{\text{cat}} \text{ s)}^{-1}$, while the oxidation rates of toluene on Pd/m- ZrO_2 and t- ZrO_2 at 4000 ppm were 25.4 and $110.6 \text{ } \mu\text{mol (g}_{\text{cat}} \text{ s)}^{-1}$, respectively. The corresponding TOF of Pd/ ZrO_2 is shown in Table S3. The oxidation rates of toluene as a function of toluene on Pd/ ZrO_2 catalysts are shown in Fig. 3C and D. The activity of Pd/t- ZrO_2 was higher than that of Pd/m- ZrO_2 with a toluene concentration below 2000 ppm , on the contrary, the situation is reversed with a toluene

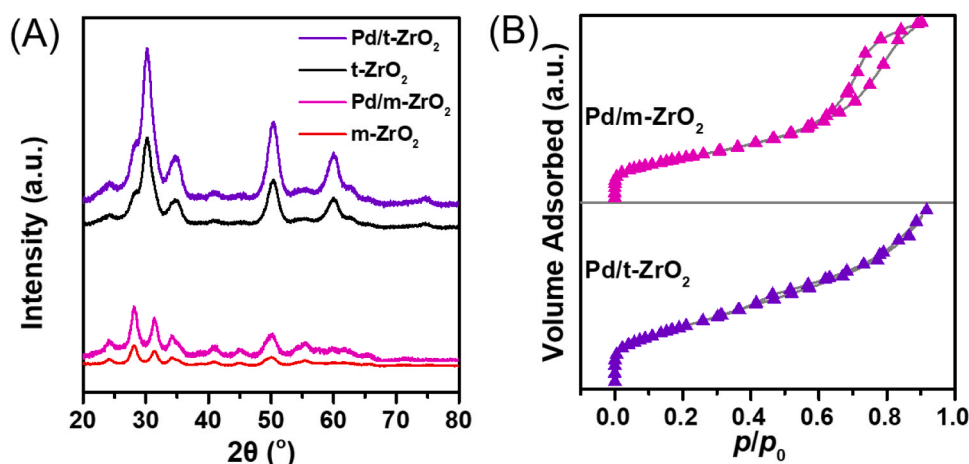


Fig. 1. (A) XRD patterns; (B) N_2 adsorption-desorption isotherm of Pd/m- ZrO_2 and Pd/t- ZrO_2 .

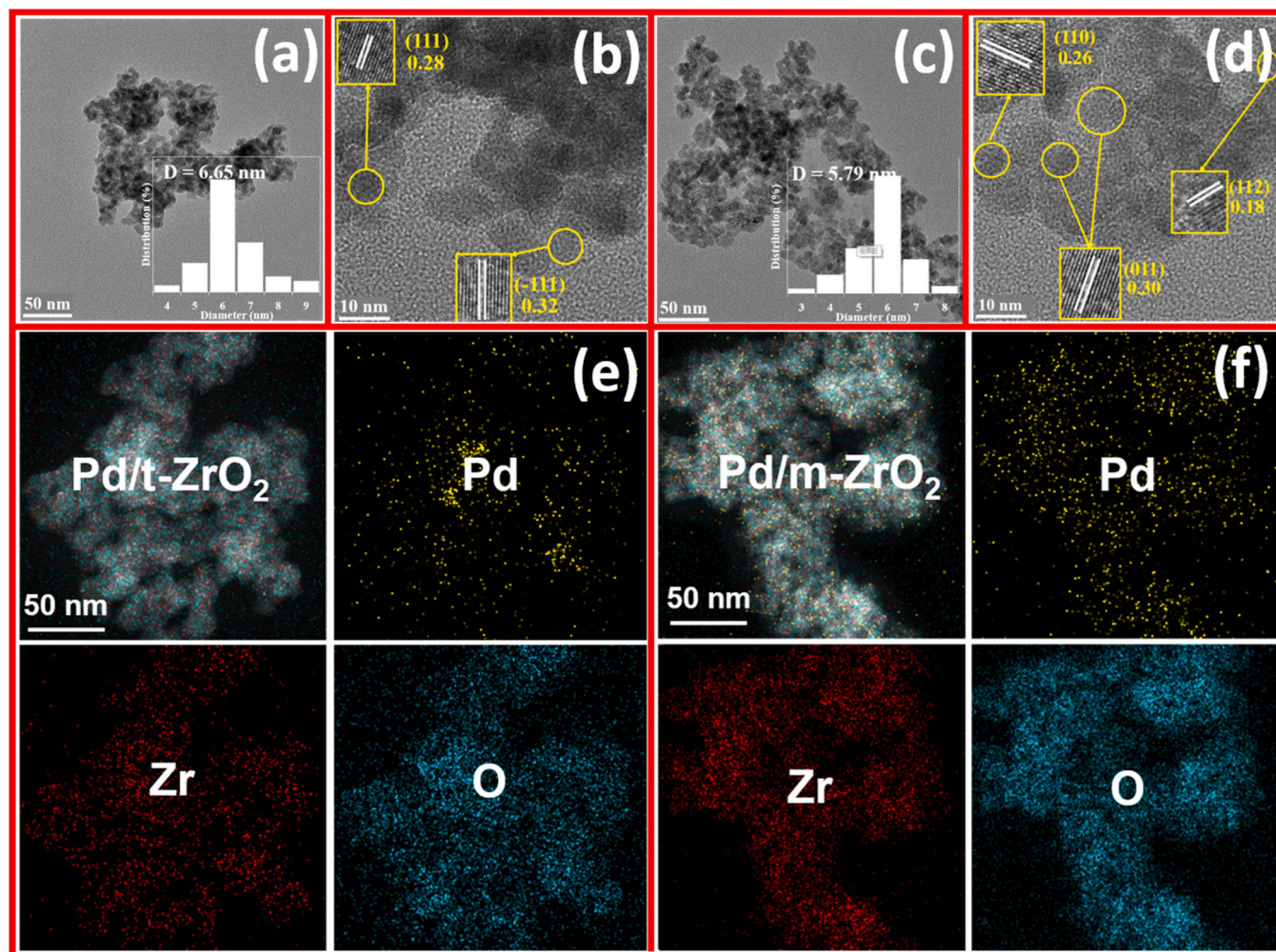


Fig. 2. TEM images of Pd/m-ZrO₂ (a) and Pd/t-ZrO₂ (c), HRTEM images of Pd/m-ZrO₂ (b) and Pd/t-ZrO₂ (d), EDS composition of Pd/m-ZrO₂ (e) and Pd/t-ZrO₂ (f).

concentration above 3000 ppm. Meanwhile, by calculating the apparent activation energies of Pd/m-ZrO₂ and Pd/t-ZrO₂ at different toluene concentrations (Table S4), it was found that Pd/m-ZrO₂ possessed the lowest activation energy (125 kJ/mol) at 4000 ppm toluene, while Pd/t-ZrO₂ exhibited the lowest activation energy at 1000 ppm toluene (103 kJ/mol). In addition, the cyclic test and long stabilities of catalysts are shown in Fig. S2 and Fig. S3. It was found that the two catalysts exhibited excellent stability under the all investigated reaction temperatures.

In order to understand the intrinsic activity of Pd/ZrO₂, the mass specific activities with respect to toluene and oxygen concentration in the kinetic region are represented. Note that the reaction order of oxygen on both Pd/ZrO₂ catalysts were 0, as shown in Fig. S4. Based on the power model, the reaction equation could be expressed as follows:

$$r = kc_{(\text{toluene})}^a$$

Where r , k , $c_{(\text{toluene})}$ and a represent toluene reaction rate, rate constant, toluene concentration and reaction order, respectively. The reaction order of toluene on Pd/t-ZrO₂ catalyst was almost 0. However, the reaction order of toluene on Pd/m-ZrO₂ catalyst was 2 at 200, 210 and 220 °C (Figs. 3C and 3D). These results indicated the key step was the toluene adsorption and activation, which resulted in the different results in catalytic activity. The different reaction orders were due to the different reaction mechanisms. The different toluene concentrations and oxygen concentrations were measured to understand the reaction mechanisms, which followed the same procedures as our previous work

[38]. But no specific mechanism could be established to illustrate all the reaction, which was probably the mixed mechanism [43,44] in the catalytic oxidation reaction. Previous references have shown that the adsorption of toluene was hinged by the redox properties of Pd [9,17]. Therefore, H₂-TPR and XPS were used to characterize redox properties of the catalyst surfaces.

3.3. Redox properties of catalyst surface

Fig. 4A shows the H₂-TPR curves of Pd/ZrO₂ and ZrO₂. The ZrO₂ samples only contained two reductions peaks in the range of 400–600 °C. Both Pd/ZrO₂ samples showed one negative and four positive peaks corresponding to the reduction peaks of different oxygen species. An inverted peak was observed, which could belong to the decomposition of PdH_x ($x < 1$) at low temperature (100 °C). During the H₂-TPR experiment, Pd first reacted with hydrogen to form palladium hydride at low temperatures [45]. As the temperature rises, the PdH_x species decomposed and produced hydrogen, resulting in inverted peaks. For the positive peaks, the peak at ca. 150 °C was assigned to the reduction peaks of PdO on the catalyst surface [30,34] and the peaks near 300 °C were regarded as the reduction peaks of Pd–O–Zr species [46]. The two peaks near 400–600 °C were assigned to surface lattice oxygen and bulk phase lattice oxygen of ZrO₂ [29]. The reduction temperatures of PdO and Pd–O–Zr species in Pd/t-ZrO₂ were lower than those in Pd/m-ZrO₂, which was probably in relation to the easier electron transfer from zirconia to palladium in Pd/t-ZrO₂. The strong interaction between m-ZrO₂ and Pd, compared with Pd/t-ZrO₂, resulted

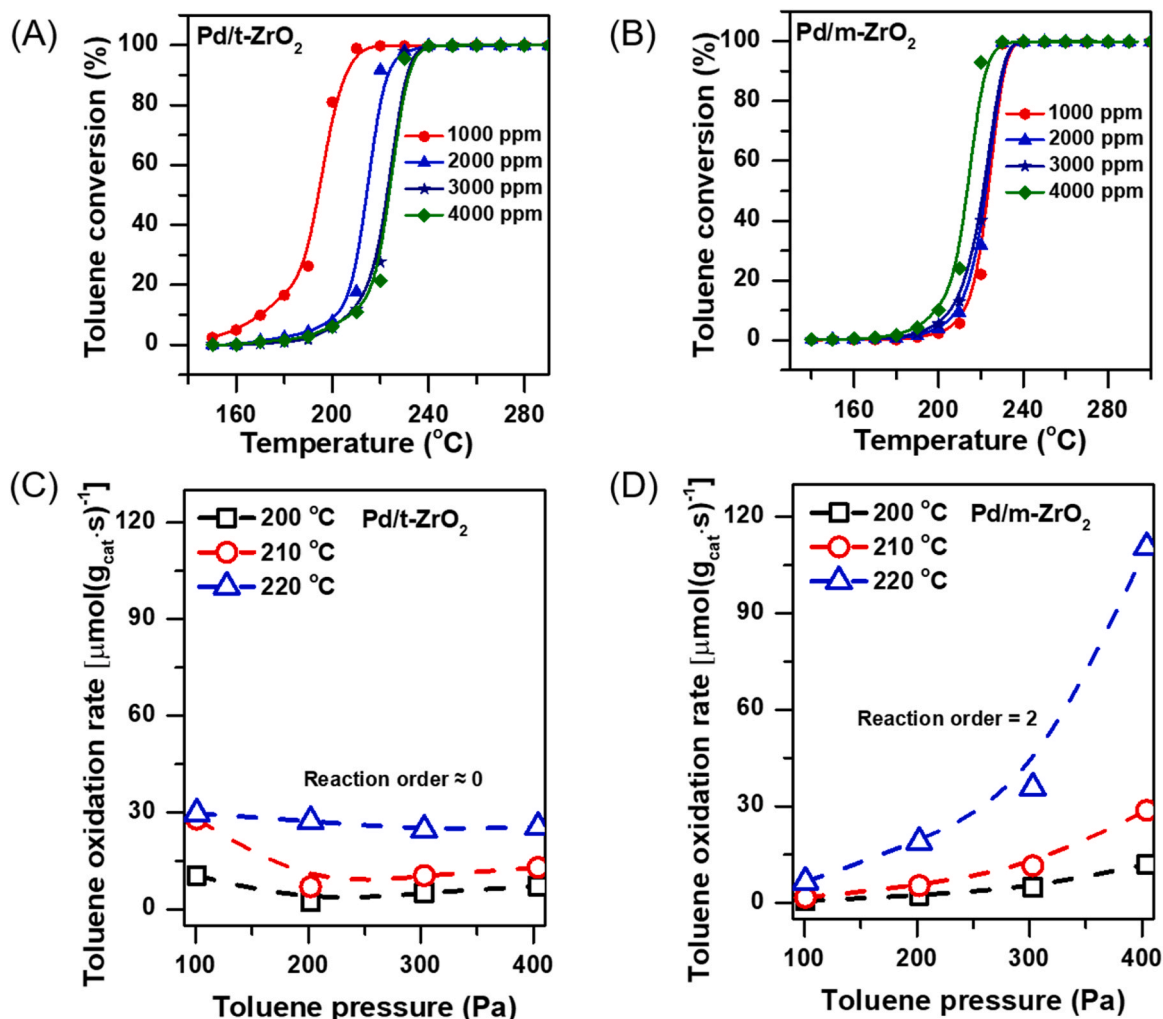


Fig. 3. The catalytic performance of Pd/t-ZrO₂ (A) and Pd/m-ZrO₂ (B) at different toluene concentrations as a function of the temperature; The relationship between toluene oxidation rate and toluene pressure of Pd/t-ZrO₂ (C) and Pd/m-ZrO₂ (D).

in the difficulty in the reduction of Pd–O. The area of the first peak belonging to surface PdO on Pd/m-ZrO₂ was 1.6 times larger than that of Pd/t-ZrO₂. Meanwhile, the area of the fourth positive peak of lattice oxygen of t-ZrO₂ was one-fold as that of m-ZrO₂, which was probably due to the migration of lattice oxygen from m-ZrO₂ to the Pd and the more formation of PdO species. From the results of H₂-TPR, it could be concluded that t-ZrO₂ resulted in the formation of highly active PdO species, while m-ZrO₂ was beneficial to the larger amount of PdO species.

The valence states and contents of various elements on the catalyst surface were measured by XPS, and the results are shown in Fig. 4C and D. The XPS spectrum of Pd 3d and Zr 3p could be divided into six peaks (Fig. 4C), which could be ascribed to Zr 3p_{1/2} (332.7 eV), Zr 3p_{3/2} (346.4 eV), Pd⁰ 3d_{3/2} (335.5 eV), Pd⁰ 3d_{5/2} (341.5 eV), Pd²⁺ 3d_{3/2} (337.7 eV) and Pd²⁺ 3d_{5/2} (343.2 eV) [4,13]. The quantitative results of XPS results are shown in Table 1. The content of Pd²⁺ in Pd/m-ZrO₂ (47 %) was higher than that in Pd/t-ZrO₂ (36 %), which was consistent with the results of H₂-TPR. The higher content of Pd²⁺ may be related to the stronger interaction between Pd and ZrO₂. H₂-TPR results showed that the higher reduction temperature of Pd–O–Zr on Pd/m-ZrO₂, which indicated the stronger interaction between Pd and m-ZrO₂ on Pd/m-ZrO₂. Meanwhile, the interaction between Pd and ZrO₂ could also affect the property of oxygen. The stronger interaction between Pd and ZrO₂ led to a more favorable oxidation state for Pd. Fig. 4D shows the XPS spectrum of O 1s. Two peaks were detected at 529.9 eV and

531.8 eV, which belonged to lattice oxygen (O_{lat}) and adsorbed oxygen (O_{ads}) [29], respectively. The ratio of O_{ads} to O_{lat} is listed in Table 1. The O_{ads}/O_{lat} ratios of Pd/m-ZrO₂ and Pd/t-ZrO₂ are 63 % and 49 %, respectively. Both the higher Pd²⁺/Pd and O_{ads}/O_{lat} were in relation to the interaction between Pd and ZrO₂ [47,48]. The higher O_{ads}/O_{lat} ratio of Pd/m-ZrO₂ could be beneficial to the activation of toluene [33]. Based on our kinetic studies, the promotional effects on the toluene activation could increase the catalytic activity, since the order of toluene was 2 in Pd/m-ZrO₂.

Fig. S5 shows the in-situ DRIFTS CO adsorption spectra over Pd/m-ZrO₂ and Pd/t-ZrO₂. The two characteristic peaks between 2000 and 2200 cm⁻¹ were the linear adsorption of CO in the oxidized state Pd (CO–Pd²⁺) and the reduced state Pd (CO–Pd⁰), respectively [48]. The two characteristic peaks between 1800 and 2000 cm⁻¹ were bridge adsorption of CO in Pd⁰ and triple hollow adsorption [49]. According to the linear adsorption of CO in the region of 2000–2200 cm⁻¹, the areal ratio of CO–Pd²⁺ and CO–Pd⁰ on Pd/m-ZrO₂ catalyst was 0.93, which was higher than that of the Pd/t-ZrO₂ catalyst (0.73), and was consistent with the results of XPS.

In order to quantify the content of the surface oxygen of catalysts, oxygen storage capacity (OSC) was measured via switching H₂/O₂ atmosphere [38]. Fig. 4B shows the TGA curves of Pd/m-ZrO₂ and Pd/t-ZrO₂ catalysts in the cycle of oxidative and reductive atmosphere. The oxygen storage capacity (OSC) of Pd/m-ZrO₂ was 638 μmol O/g_{cat}, which was more than 3-fold higher than Pd/t-ZrO₂ (178 μmol O/g_{cat}).

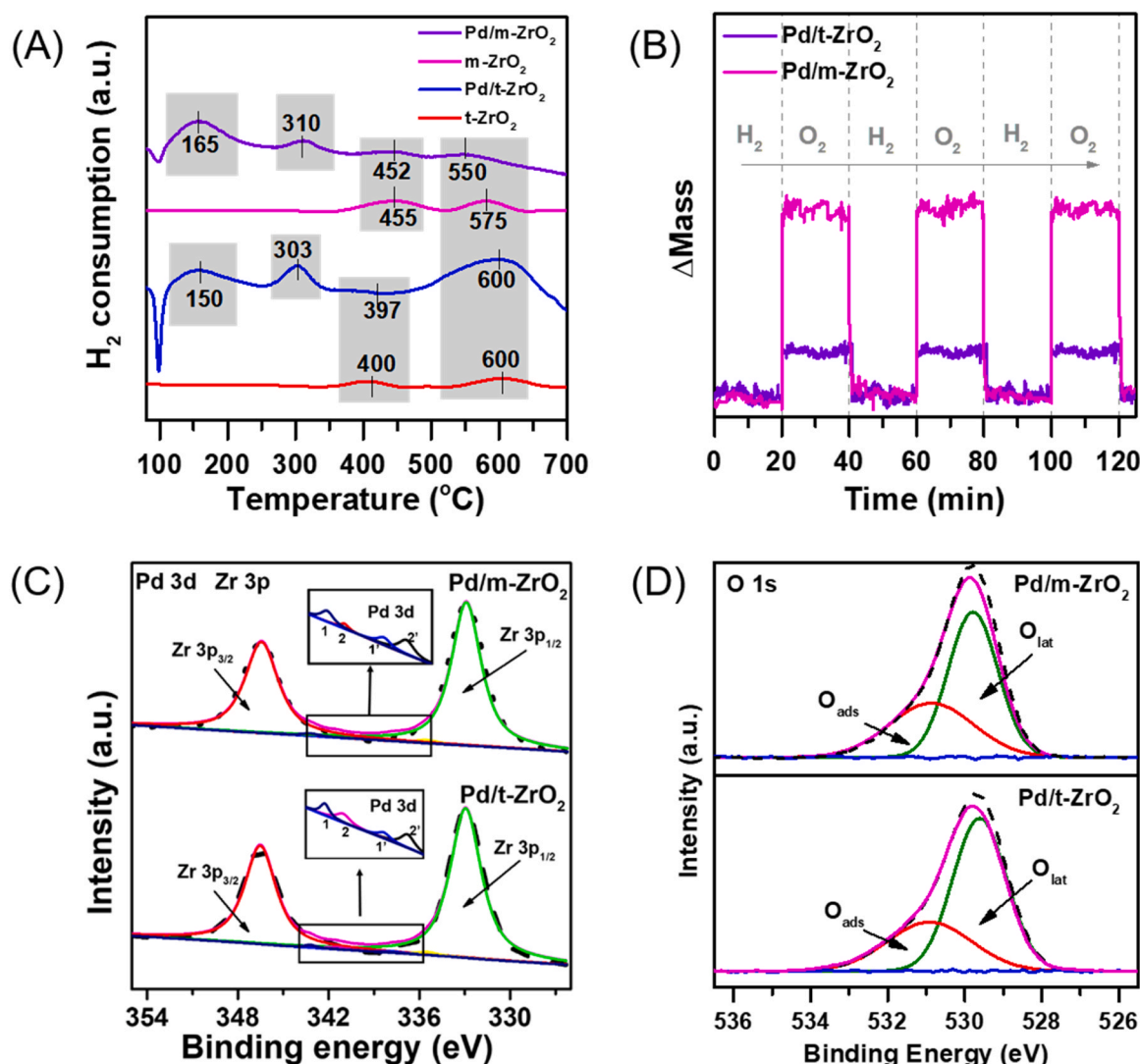


Fig. 4. H₂-TPR curves (A); Thermogravimetric (TG) spectrogram (B) when oxygen and hydrogen were introduced alternately; XPS spectra of Pd and Zr (C) (peak of Pd²⁺ 3d_{3/2} (0), Pd²⁺ 3d_{5/2} (1'), Pd⁰ 3d_{3/2} (2) and Pd⁰ 3d_{5/2} (2')); XPS spectra of O (D).

The OSC of m-ZrO₂ and t-ZrO₂ were 595 and 141 μmol O/g_{cat} (Fig. S6), respectively. These results indicated that the oxygen in m-ZrO₂, which participated in the reaction, was more than 4-fold of that in t-ZrO₂. Meanwhile, the ORR of Pd/m-ZrO₂ (0.53 μmol O/g_{cat}/s) was nearly twice of Pd/t-ZrO₂ (0.29 μmol O/g_{cat}/s). The large amount of oxygen migration resulted in a positive effect on the formation of active PdO_x species on m-ZrO₂, which enhanced the catalytic activity at the high toluene concentration.

The temperature-programmed surface reaction (TPSR) was investigated in the absence of O₂ (Fig. S7), and mass spectrometry was used to detect all the effluent reaction gas. Only CO₂ and H₂O, and no other intermediates was observed. According to the results, it was concluded that the intermediates existed on the catalyst surface at an adsorbed state. In addition, the absence of O₂ in the TPSR results indicated that the reaction mechanism of toluene combustion over Pd/ZrO₂ follows the Mars-van Krevelen (MvK) mechanism. Meanwhile, it could be concluded from the amount of CO₂ ($m/z = 44$) over Pd/m-ZrO₂ that Pd/m-ZrO₂ contained more active oxygen species than Pd/t-ZrO₂ catalyst.

3.4. In situ-DRIFTS

In situ-DRIFTS experiments were used to study the reaction pathway of toluene on the catalyst. The kinetic studies showed that the reaction

rate was only related to the toluene pressure rather than oxygen pressure in the feed gas. Thus, we could deduce that the oxygen of catalyst was vital for the toluene combustion. Moreover, It is widely accepted that the oxygen needed for the toluene reaction was those from the palladium oxide species [31,50,51], which was formed by the migration of surface lattice oxygen of zirconium oxide [20]. In order to understand the role of oxygen of catalyst, toluene was passed into a catalyst in the absence of oxygen to detect the reaction mechanism of toluene oxidation process.

Fig. 5A and C show the in situ-DRIFTS spectrum of Pd/m-ZrO₂ and Pd/t-ZrO₂ in the presence of 1000 ppm toluene as a function of time. The bands at 3689, 3587 and 3566 cm⁻¹ were attributed to the tensile vibration peaks of hydroxyl groups on the surface of the catalyst [28,38,52]. The peaks at 1688, 1733, 1653 and 1648 cm⁻¹ were assigned to C=O tensile vibrations of aldehydes [38]. The peak at 1260 cm⁻¹ was associated with the C-O tensile vibration peak of benzyl alcohol group [53,54]. The peaks at 1496 and 1508 cm⁻¹ were attributed to the typical skeleton (C=C) vibration of the toluene aromatic ring [55]. The peaks of 1395, 1338, and 1540 cm⁻¹ were ascribed to the typical vibration of carboxylic acid species (symmetric stretch vibration and asymmetric stretch vibration) [5,56], and the peak of 1400 cm⁻¹ was considered to be the typical peak of mono-dentate carboxylate [57,61]. The bands at 1363 and 1473 cm⁻¹ were assigned to the (CH₃) symmetric and asymmetric deformation vibrations of the methyl (CH₃) group [6,58,59]. The

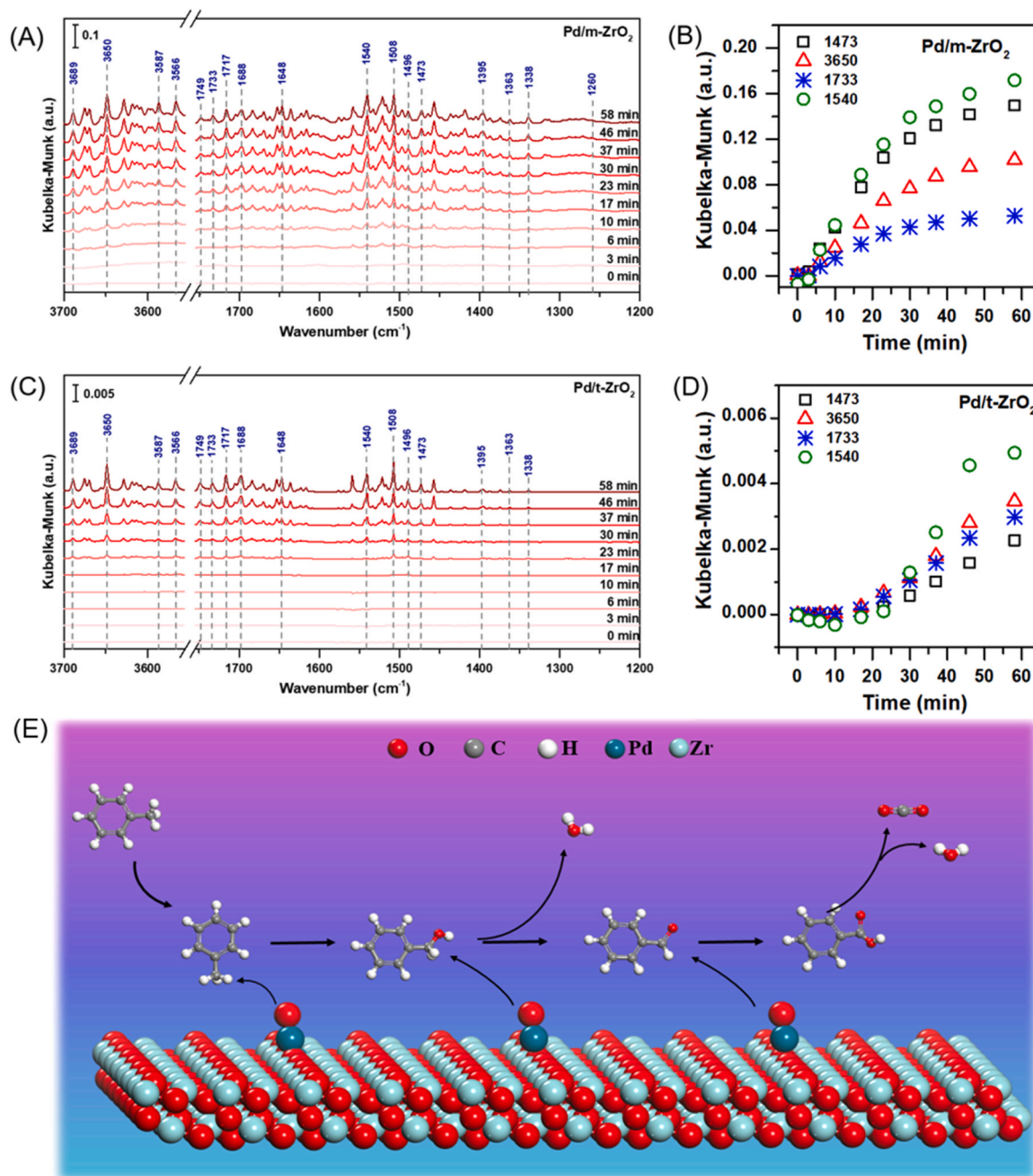


Fig. 5. Time-resolved DRIFT spectra showing accumulation of surface species over Pd/m-ZrO₂ (A) and Pd/t-ZrO₂ (C) catalyst; The IR band heights of the surface key species over Pd/m-ZrO₂ (B) and Pd/t-ZrO₂ (D) catalyst; reaction pathway of catalytic combustion of toluene on Pd/ZrO₂ (E).

bands of 1749 and 1717 cm⁻¹ were associated with the C–O–C characteristic peaks of anhydride species [19,55,60] and the C=O vibration peaks of ketones, respectively. All these intermediate species and corresponding peak positions are shown in Table 2. For both Pd/ZrO₂ catalysts, the characteristic peaks of toluene (1508 cm⁻¹) and benzyl alcohol (3650 cm⁻¹) first appeared, indicating that toluene was initially adsorbed on the surface of the catalyst and oxidized to benzyl alcohol. Then the characteristic peak of benzaldehyde (1733 cm⁻¹) and benzoic acid (1540 cm⁻¹) gradually appeared indicating that benzyl alcohol was further oxidized to benzaldehyde, regenerated into benzoic acid, and finally turned into CO₂ and water. It should be noted that the intensity of adsorbed species of Pd/m-ZrO₂ was ca. 20 times than that of Pd/t-ZrO₂, illustrating more adsorption of toluene on Pd/m-ZrO₂ than Pd/t-ZrO₂, which was consistent with the kinetic studies. Moreover, from the intensity of IR species, the rate-determining step in the whole reaction

Table 2

Assignment of DRIFTS bands for the adsorbed species [5,28,38,52–61].

Vibrations (cm ⁻¹)	Assignment
3689, 3587, 3566	O–H stretching vibration peaks of surface hydroxyl groups
3650, 1260	O–H vibrational peaks and C–O stretching vibrational peaks of benzyl alcohol groups
1688, 1733, 1653, 1648	C=O stretching vibration peak of benzaldehyde
1496, 1508	C=C stretching vibration peak of benzene ring skeleton
1338, 1395, 1400, 1540	Correlation peaks for typical benzoic acid species
1363, 1473	(CH ₃) Symmetric and Asymmetric Stretching Vibrations of the CH ₃ -Group
1717	C=O vibration peaks of ketones
1749	C–O–C characteristic peaks of anhydride species

could be deduced. The characteristic peak of each species was related to its rate of production and consumption. By analyzing the intensity with respect to time, it was found that the intensity of the characteristic peak of benzaldehyde increased gradually and plateaued at ca. 40 min, which indicated that the oxidation rate of benzyl alcohol to benzaldehyde was equal to that of benzaldehyde to benzoic acid. However, the strength of the benzoic acid characteristic peak increased steadily at first and then increased gradually even at 60 min, suggesting that the consumption rate of benzoic acid was lower than the production rate. To sum up, the oxidative decomposition of benzoic acid may be the rate-controlling step in the catalytic toluene oxidation. Similar results were also observed by Li et al. [6]. Based on the *In-situ* DRIFTS results, the oxidation process of toluene is shown in Fig. 5E. At the first step, toluene molecules were adsorbed on the surface of the catalyst, and the active PdO species on the surface reacted with the adsorbed toluene to produce benzyl alcohol. It was then oxidized by PdO to generate benzaldehyde, which was further oxidized to produce benzoic acid and finally converted into CO₂ and H₂O.

3.5. A DFT study for reactivity of Pd–O on Pd/ZrO₂

Previous results, i.e., kinetic studies, XPS and H₂-TPR, showed that the oxygen of the catalyst was vital for toluene combustion. Therefore, theoretical models of Pd/ZrO₂ catalysts were established to study the properties of Pd–O bonds via calculating the desorption energy (E_{des}) and the partial density of states (PDOS) of O upon O–Pd/ZrO₂ [62]. The optimized structures of m-ZrO₂ ($\bar{1}11$) and t-ZrO₂ (101) surface were used to construct the O–Pd/ZrO₂ system (Fig. 6A). It was calculated that the maximum desorption energies of O atoms in O–Pd/m-ZrO₂ and O–Pd/t-ZrO₂ were 1.46 and 0.53 eV, respectively (Table 3), implying that Pd–O species on the surface of t-ZrO₂ were more reducible, which was consistent with the experimental results. PDOS of the 2s and 2p orbitals of O upon Pd/m-ZrO₂ and Pd/t-ZrO₂ (Fig. 6B) illustrated that electron density near the Fermi level of O atom upon Pd/t-ZrO₂ was higher. The energy-weighted average ϵ (p-band center) [42,63] of the active O adsorbed on Pd/t-ZrO₂ was -3.03 eV, while the p-band center ϵ of the active O adsorbed on Pd/m-ZrO₂ was -3.26 eV, implying that the active O upon Pd/t-ZrO₂ was more unstable than Pd/m-ZrO₂. These results were in agreement with the electron transfer clarified by XPS and CO-DRIFTS. All these provided a basic understanding of O–Pd on Pd/ZrO₂ via the desorption energy and PDOS.

4. Conclusions

In this work, the effect of ZrO₂ crystalline phases on Pd/ZrO₂ catalysts was studied for toluene combustion. Pd/t-ZrO₂ showed excellent

Table 3

Total energies of systems used to calculate the oxygen desorption energy (E_{des}) upon the m-ZrO₂($\bar{1}11$)-(1 × 1) surface and t-ZrO₂(101)-(2 × 1) surface.

Surface	Adsorption site	E (Pd+m-ZrO ₂) (eV)	E (O+Pd+m-ZrO ₂) (eV)	E (O) (eV)	E_{des} (eV)
m-ZrO ₂ ($\bar{1}11$)-(1 × 1)	1	−228.34	−233.89	−4.93	0.62
	2	−227.50	−233.89		1.46
	3	−228.36	−233.92		0.63
	4	−227.93	−233.38		0.52
t-ZrO ₂ (101)-(2 × 1)	1'	−229.86	−235.32	−4.93	0.53
	2'	−229.86	−235.14		0.35
	3'	−229.81	−234.90		0.16
	4'	−229.50	−234.78		0.35

catalytic performance at low concentration of toluene, while Pd/m-ZrO₂ exhibited superior catalytic performance at high toluene concentration. Kinetic studies showed that the reaction order of toluene on Pd/t-ZrO₂ was 0 and that on Pd/m-ZrO₂ was 2. Meanwhile, the reaction order of oxygen on both Pd/ZrO₂ was 0. H₂-TPR, XPS and OSC indicated that t-ZrO₂ contributed to the formation of highly active PdO species, while m-ZrO₂ was beneficial for the higher content of PdO species. The catalytic activity was correlated with comprehensive effect between the amount and chemical properties of PdO on the surface of the catalysts. DFT results demonstrated that electron density near the Fermi level and p-band center of O atom on Pd/t-ZrO₂ were higher than that of Pd/m-ZrO₂, thus weakening the Pd–O bond. *In situ*-DRIFTS results revealed the reaction path of toluene oxidation: gaseous toluene was firstly adsorbed on the surface of the catalyst and then subsequently oxidized to benzyl alcohol, benzaldehyde, benzoic acid, and finally completely oxidized to CO₂ and H₂O. These results revealed the influence of the crystal effect of the support on the catalytic combustion reaction via the combination of kinetic studies, DRIFTS and DFT theory in depth, providing a guideline for the design and development of high performance catalysts for VOCs combustion.

CRediT authorship contribution statement

Decun Luo: Formal analysis, Investigation, Writing – original draft, Visualization. **Ziyu Tang:** Visualization, Data curation. **Xiyang Yu:** Visualization. **Tao Zhang:** Data curation, Validation. **Chun-Ran Chang:** Supervision, Funding acquisition. **Zhun Hu:** Project administration, Funding acquisition, Supervision, Writing - review & editing.

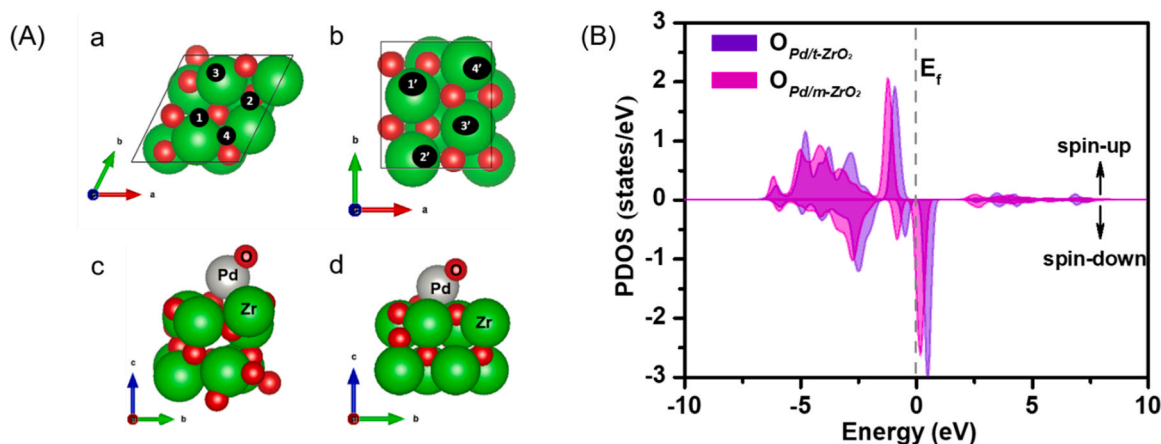


Fig. 6. (A) Adsorption sites Pd–O species upon m-ZrO₂ (a) and t-ZrO₂ (b), and the modes of Pd/m-ZrO₂ (c) and Pd/t-ZrO₂ (d). (B) PDOS of the 2s and 2p orbitals of O upon Pd/m-ZrO₂ and Pd/t-ZrO₂.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

The data that has been used is confidential.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2023.123117.

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